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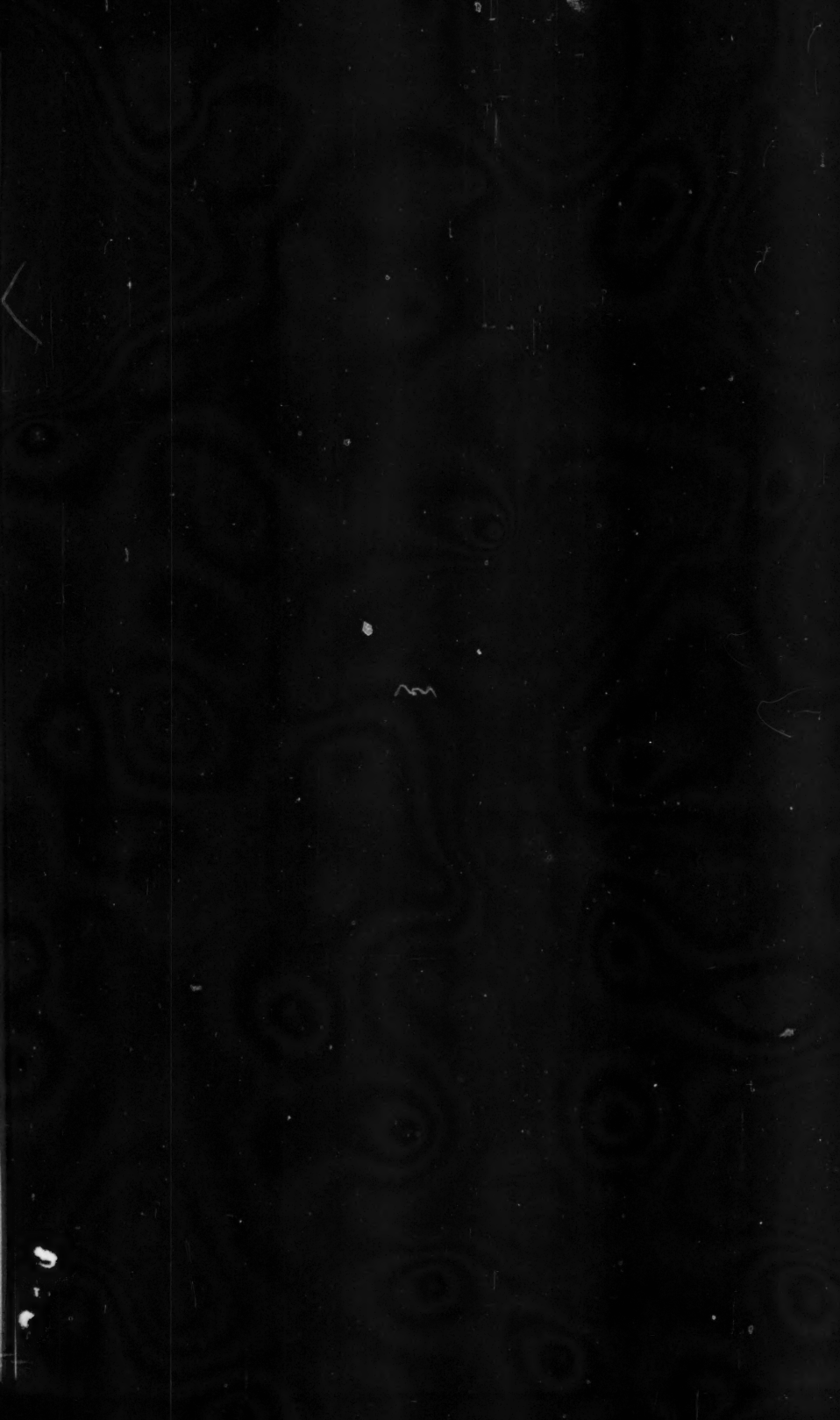
By P. W. BRIDGMAN.

INVESTIGATIONS ON LIGHT AND HEAT MADE AND PUBLISHED WITH AID FROM THE
RUMFORD FUND.

(Continued from page 3 of cover.)

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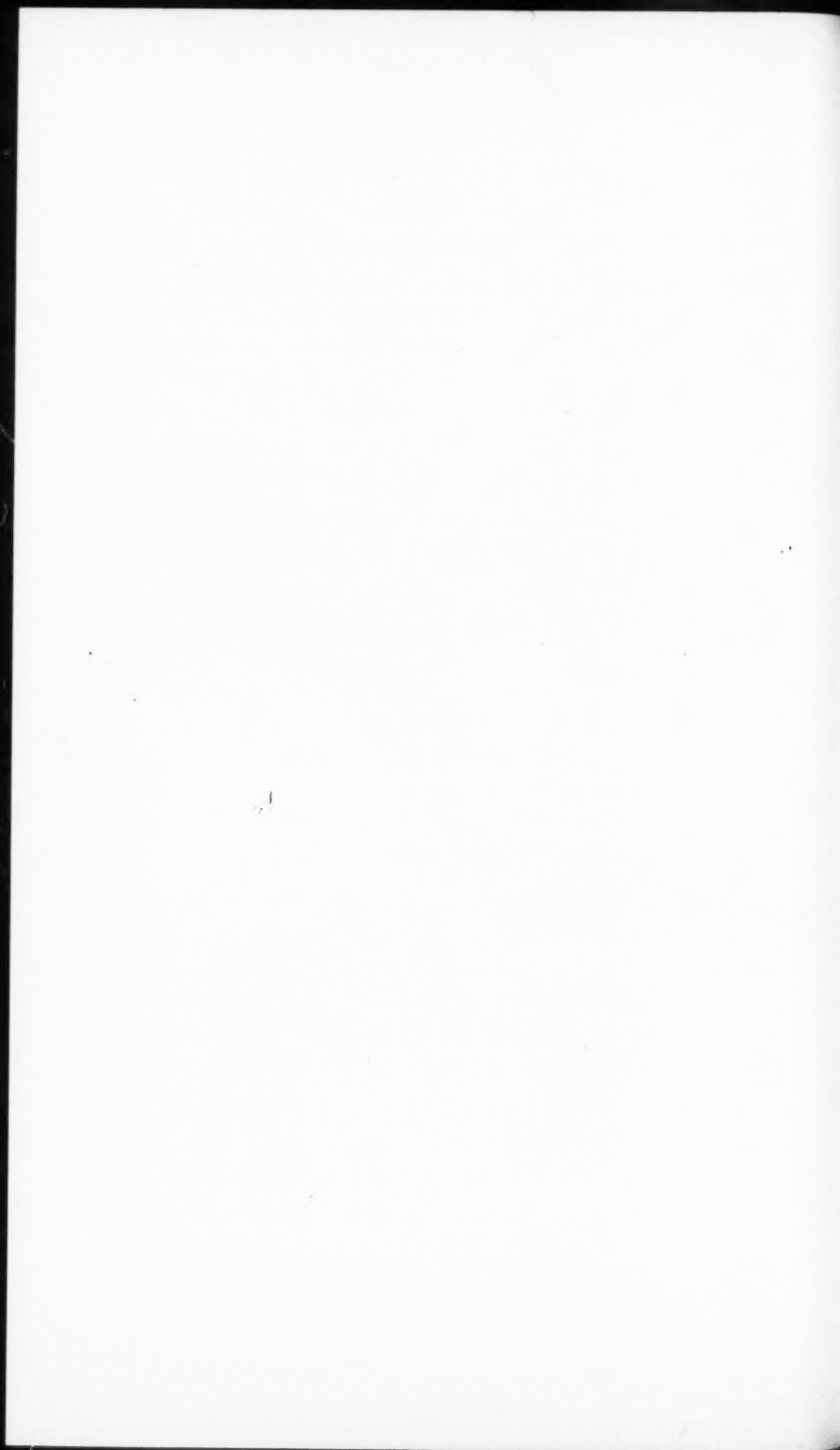
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CONTENTS.

Introduction	71
Apparatus and Technique	73
Detailed Data	80
Resistance of Gold, Silver, and Iron	80
Resistance of Black Phosphorus	82
Resistance of Single Crystal Tellurium	85
Resistance of Copper Sulphide	89
Compression and Thermal Expansion of Lithium	91
Compression and Thermal Expansion of Sodium	93
Compression and Thermal Expansion of Potassium	95
Discussion	96
Summary	99

INTRODUCTION.

A number of the phenomena which have presented themselves in a rather extensive survey of the properties of matter up to 12000 kg/cm² have proved to have features of sufficient significance and interest to justify the serious attempt to extend materially the pressure range. In this paper measurements are presented of such phenomena up to 20000 kg/cm². The electrical resistances of black phosphorus and of tellurium are studied; both of these substances had been found to have an abnormally high decrease of resistance with increasing pressure.¹ It was of interest to find whether the resistance of these materials could be forced by sufficiently increasing pressure to approach the resistance of the true metals. An investigation of other semi-conductors suggests itself in view of recent advances in our theoretical understanding of the nature of the mechanism of conduction; it would appear that in general there is some ground for the expectation that at least some semi-conductors can be forced into something like the metallic state by very high pressures, and that therefore a systematic investigation of such substances to the highest

attainable pressures should be of interest. There are very few measurements on such substances over the lower pressure range, so that the grounds do not exist for selecting those substances which most probably will show significant high pressure effects. Furthermore, the difficulty of the investigation is increased by the fact that not many semi-conductors can be obtained in a geometrical form suitable for the measurements. The only course is, therefore, the empirical one of trying all the feasible semi-conductors. A beginning of such an exploration is presented here in measurements on CuS_2 , which is easy to obtain in massive form. Finally, measurements have been made on the volume as a function of pressure and temperature of the three alkali metals, lithium, sodium, and potassium. In the last few years theoretical understanding of the metallic state has advanced sufficiently to permit a calculation of the compressibility with some success, so that a knowledge of the behavior of these especially simple metals is desirable over as great a range of pressure as possible. For some time it has, furthermore, been evident that a knowledge of the thermal expansion also of these metals would be useful, but such determinations have offered the greatest experimental difficulties, and hitherto I have not succeeded in making any good measurements for these substances, even in the lower pressure range. The primary purpose of the present measurements was to yield reliable values for the thermal expansion, and now after many attempts I believe that I have obtained values which give the essential broad features of the behavior of thermal expansion up to 20000, although the accuracy is not greater than a few per cent, and there are finer details which it would have been desirable to establish.

In comparing the present compressibility measurements over the wider pressure range with those previously made, a serious error was uncovered in my early published values for compressibility.² The correction for the second order effect in converting linear into volume compressibility was applied with the wrong sign in nearly all the measurements published through 1923. The compressibility at low pressures is unaffected by this error, but the volume changes at the maximum pressure were too large by a fractional amount equal to twice the change of linear dimensions themselves. The error is thus largest for the most compressible materials and for the highest pressures; at 12000 kg/cm^2 the error varies from 1 per cent for iron to 14 per cent for potassium. The corrected values are to be given in detail in another paper.

APPARATUS AND TECHNIQUE.

A number of modifications were necessary in the apparatus and technique. In the first place, a hydrostatic press of larger capacity for producing the pressure was necessary. The new press was of about twice the capacity of the old one, the diameter of the piston being 3.5 inches, against 2.5, yielding, with a maximum working pressure of 15000 lb/in² on the 3.5 inch piston, a total force of about 140000 lb. This could be concentrated on a high pressure piston usually about 0.5 inches in diameter, thus allowing a maximum pressure in the high pressure cylinder of the order of 50000 kg/cm², making no allowance for friction.

Formerly the high pressure part of the apparatus consisted of three parts: a cylinder in which pressure was produced and in which was situated the manganin pressure gauge, a connecting pipe, and a cylinder containing the particular specimen under measurement. The apparatus now consisted of a single cylinder, turned with a shoulder on the upper end, by which it was retained in the lower head of the press, the bulk of the cylinder projecting beyond the press as indicated in Figure 1. The temperature bath was brought up around the

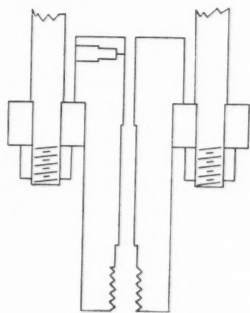


FIGURE 1. Section of the high pressure cylinder mounted in the lower end of the press.

cylinder, the liquid in the bath standing nearly to the top of the cylinder and covering the lower head of the press and the lower ends of the tie rods. The cylinder, except for a by-pass at the upper end by which it was charged as usual to an initial pressure of 2000 or

3000 kg/cm², was pierced with a single longitudinal hole. This is a departure, made necessary by the demand for maximum strength, from the previous design, in which the manganin gauge was let in through a hole at the side. The leads for the manganin gauge were now brought in at the bottom, along with the leads necessary for the potentiometer measurements, as will be described later.

An alloy steel was used for the cylinder, capable of giving higher physical properties than that which had been formerly used. Formerly a Cr-Va steel of approximately the analysis SAE 6150 was used, giving a maximum tensile strength of 225,000 lb/in². This was now replaced by a steel made by the Carpenter Steel Co. under the designation "S-M," and analyzing approximately 0.60% C, 0.75% Mn, and 1.90% Si. It may be heat treated to give a tensile strength as high as 320,000 lb/in², and has the remarkable property of showing considerable elongation even when treated to give as high a tensile figure as this. For the high pressure cylinder this steel was quenched into water from a temperature of 900° C, and then drawn at a temperature of 400° C, when it showed a Rockwell C hardness of 48, just soft enough to permit enlarging the hole with a reamer after the usual preliminary stretching. The stretching was usually done with lead, as before. The maximum pressure of the preliminary treatment was about 30000 kg/cm² for a cylinder to be used regularly to 20000, and the stretch of the interior under this preliminary treatment might be as much as 0.06 inch on an initial internal diameter of 0.44 inches and external diameter of 3.8 inches. After the preliminary stretching one or two of the cylinders were subjected to a low temperature anneal, without any very distinct evidence of improvement. The life of the cylinder was capricious, cylinders having broken after only a few hours use at 20000, while one or two have had a life of about 30 hours total exposure to the extreme pressure of 20000. Rupture may occur at pressures materially less than the maximum previous exposure. In all, five cylinders were used in the measurements to be described here.

The pistons were made of a special chrome ball bearing steel, left glass hard; and seldom gave trouble. Because of the violence of the failure of glass hard steel under compressive load, however, it is necessary to use adequate protecting shields in case of failure of the piston. The high pressure piston was packed with a plug of the same mushroom design, using the principle of the unsupported area, as has been used previously.³ Failure of these packing plugs by pinching-off

of the unsupported stem was at first fairly frequent, but has been minimized by the use of a steel made especially for cold chisels, possessing great toughness combined with high strength, by avoiding reentrant sharp angles, and by avoiding the use of soft solder in attaching the soft packing washers of brass or copper to the mushroom. This last seems to be an important point; apparently tin ultimately gets forced by high pressure into the pores of the steel, the process being assisted by the natural chemical affinity of tin and steel, and failure ultimately occurs by the analogue of the amalgamation failure previously found with mercury at a pressure of a few thousand kilograms.

The packing of the pistons is becoming one of the more serious problems in considerably extending the pressure range, and some simple device which will avoid the pinching off effect is desirable. I have had no luck with the simple solid rubber plug used by Poulter and by Imperial Chemical Industries Limited. This may be suitable if the transmitting liquid is highly viscous, but if the liquid is of low viscosity I have found that leak invariably occurs in the neighborhood of 10000 kg/cm^2 . In the present experiments it was necessary to use a liquid of the lowest possible freezing point and lowest possible viscosity; iso-pentane was the liquid so employed. It has a high initial compressibility, but this disadvantage was obviated by the initial charging through the by-pass.

The details of the method of bringing in electrically insulated leads had to be modified. The leads were now all brought through a single plug at the bottom of the cylinder; there were four such insulated leads, one for the manganin gauge coil, and three for leads to the potentiometer by which the resistance of the specimen was measured, the fourth potentiometer lead and the other lead to the gauge coil being grounded to the cylinder. The insulated leads were made of piano wire 0.010 inches in diameter. The mica washers previously used were now replaced with Solenhofen limestone, as has been used at the Geophysical Laboratory in Washington, for greater strength; furthermore the limestone cylinder was embedded in a brass sleeve which flowed sufficiently around it to prevent cracking by concentration of stress at the unavoidable local geometrical irregularities. The rubber washers by which the liquid was prevented from leaking around the stem were now replaced by a double washer, artificial rubber (Duprene) at the end next the liquid, and soft natural rubber below it. The Duprene is not attacked by iso-pentane, but is not

quite soft enough to give complete freedom from leak at the lower pressures, which is ensured by a thin layer of natural rubber. The soft packing on the mushroom plug has also been made of Duprene in these experiments with advantage, there being a marked improvement in the wearing qualities.

The general design of the plug carrying the insulated leads was radically altered; the proportions of the holes carrying the packing around the piano wire stems were so changed as to give a considerably greater ratio of length to diameter, and the plug itself was not made integral, as before, with the screw by which it was retained in the cylinder, but was a separate piece. This permitted the plug to be made much shorter, a change which greatly facilitated construction by avoiding the long accurately placed holes of small diameter demanded by the former method of construction.

The measurements of electrical resistance described in the following were made by the same potentiometer method that has been used in much of my previous work, and no further description is necessary.

The changes of dimensions of the alkali metals were measured in a piezometer of the same general design as that formerly used, but differing in detail. Attached to the specimen is a fine wire of high specific resistance, which moves over a contact fixed to the envelope containing the specimen as the dimensions of the specimen change under changes of pressure and temperature. Potentiometer measurements of the resistance of the wire between a point fixed to it and the sliding contact permit a calculation of the amount of motion, and thus the changes of dimensions of the specimen relative to the envelope. The distortion of the envelope is assumed to be known from previous measurements. Actual measurements of the compressibility and thermal expansion of steel have been made only up to 12000 kg; the results assumed here up to 20000 were obtained by extrapolating with the same second degree formulas which were adequate to represent the results over the 12000 kg range. This procedure seems safe enough in view of the small departure from linearity in the range up to 12000, and the smallness of the volume changes in steel compared with the alkali metals.

One very serious source of difficulty was permanent changes in the dimensions of the specimens, the transmitting medium becoming viscous enough under pressure to deform permanently metals as soft as these alkalis. The difficulty was minimized by changing the pressure very slowly, and by suitably varying the dimensions of the

specimens. The specimen of lithium, which is mechanically the hardest of the three, was 5.8 cm long and 6.0 mm in diameter; the sodium intermediate in softness, was 2.5 cm long and 8.7 mm in diameter, and the potassium, softest of the three, 1.27 cm long, and 8.7 mm in diameter. The compressibility increases from lithium to sodium to potassium, so that in spite of the shorter length of the potassium, the relative change of dimensions of all three was roughly the same.

From the point of view of simplicity of manipulation it would have been very much to be preferred to obtain the thermal expansion as a function of pressure from the difference of isotherms, each described over the entire pressure range. Measurements were desired at five temperatures, 0°, 30°, 52.5°, 75°, and 95°, so that this would have involved describing five isotherms to 20000 with practically perfect recovery of the zero, if thermal expansions were to be obtained by difference. In spite of many attempts, such perfection was not obtained. It was not difficult to describe a single isotherm with sufficiently small permanent distortion to give the isothermal change of volume with small error, but successive isotherms always involved sufficient permanent distortion to introduce large percentage errors into the relatively small differential thermal expansions. Two different procedures were therefore finally adopted for getting compressibility and thermal expansion. The compression at 0° C was first determined by describing an isotherm over the entire pressure range, up and back, at this temperature. There was an advantage in working at 0° because the metals were mechanically least deformable at this temperature. The thermal expansions at four mean pressures, 5000, 10000, 15000, and 20000 were then obtained by successive readings at the five temperatures, up and down, the position of the piston being held fixed during a temperature excursion and therefore the pressure constant, except for the small changes due to the thermal expansion of the transmitting liquid. Distortion of the specimen under these conditions was practically eliminated, because of the very small movement of the transmitting liquid; and the recovery of the initial reading on returning to 0° was always very close. In any event, the mean of the readings with increasing and decreasing temperature should give the thermal expansion with sufficient accuracy. The manipulations involved in this procedure were slow, demanding for each reading the changing of the temperature of the bath and then waiting for temperature equilibrium; about six hours were necessary for the determinations of thermal expansion at a single mean pressure,

as compared with two or three hours sufficient for an isotherm over the entire pressure range. Such long manipulations were undesirable, particularly at the higher pressures, because of shortening of the life of the cylinder and the possibility that the entire series of measurements would be ruined by an explosion. There seemed no way of avoiding this procedure, however, and most fortunately all the final thermal expansion measurements on the three metals, as well as the calibrating blank runs, were made with the same cylinder. This cylinder showed, however, toward the end of the measurements, unmistakable evidences of approaching failure.

The thermal expansions as directly determined were the differential expansions with respect to the steel envelope. In reducing to absolute expansion, the values of the thermal expansion of iron implicitly contained, but not explicitly stated, in the former measurements of compressibility at two different temperatures were assumed to be correct, and furthermore, as already explained, the results were extrapolated from 12000 to 20000 by the same second degree formula that had sufficed in the range up to 12000. This precise assumption is not a matter of much importance, however, because the thermal expansion of iron is small compared with that of the alkali metals, and the variation with pressure is relatively small. The figures assumed for the linear expansion of iron were 0.0000120 at atmospheric pressure and 0.0000110 at 20000. In making the final computations it was necessary to use corrections which had been determined from a run in which the specimen of alkali metal was replaced by a piece of pure iron. The reason for this was that it would not have been safe to assume that the thermal expansion of all parts of the envelope, which consisted of hard and soft steel and in addition a thin mica washer for insulation, was the same as that of pure strain-free iron. The corrections were so determined as to make the results with the blank run agree with the results assumed for pure iron. As a matter of fact, the corrections so found were of little importance.

In addition to permanent distortion in the specimens, another serious difficulty in getting accurate measurements was in the slight fluctuations in the manganin gauge. The difficulty was probably accentuated by the fact that the gauge was subjected to the same changes of temperature as the specimen. In the former measurements to 12000 the gauge was mounted in a separate cylinder, and maintained continually at room temperature, independent of the temperature of the specimen. The necessity for making the apparatus all

in one piece now demanded that the gauge have the same temperature as the specimen. This demanded in the first place a determination of the pressure coefficient of the gauge as a function of temperature. This was done by comparing the gauge at each of the five temperatures against a standard manganin gauge, which had been calibrated in the regular way against the freezing pressure of mercury at 0°C and which was maintained continuously at room temperature. This comparison was made up to 12000 kg/cm^2 . In this range the high pressure gauge was linear against the standard gauge at each temperature. The pressure coefficient is not, however, quite a linear function of temperature, but increases less rapidly at the higher temperatures. The coefficient was found to increase by 1.30 per cent from 0° to 50° , and by 2.04 per cent from 0° to 95° . Partly, perhaps, because of the temperature changes, partly because of the greater pressure range, partly because the wire was of smaller diameter than that which had been previously used, 0.076 mm in diameter instead of 0.134 , so that viscous drag by the transmitting medium is greater, and partly because the manganin itself is from a different source, being of recent American manufacture rather than of German manufacture of 40 years ago, the permanent zero changes after application of pressure were inclined to be much greater and more capricious than in the previous work. In fact, the changes found at first were sufficiently great to affect seriously the accuracy of the thermal expansion measurements. A special process of seasoning was therefore adopted; this consisted in maintaining the wire at a temperature of 130°C continuously for a week, except that for a few minutes every morning the coil was cooled to the temperature of solid CO_2 . This treatment was effective in reducing the zero wandering to a harmless amount. Thus, after the series of thermal expansion measurements of lithium and potassium, the zero had changed by an amount equivalent to 17 kg/cm^2 , 0.085 per cent of the maximum range. The zero change after the runs with sodium was greater, but there was internal evidence showing that the change had mostly occurred at one definite place, so that correction could be easily applied for it.

The extension of the pressure scale from 12000 to 20000 by linear extrapolation of the manganin gauge readings is an unsatisfactory feature, but one which appeared necessary. However, it was possible by two lines of attack to convince oneself that the error so introduced is probably of negligible importance. The problem here is somewhat like that of finding a suitable method of extending temperature

measurements into the region close to 0° Abs. and the methods adopted are also somewhat similar. If the extrapolated scales given by different phenomena agree, one may have considerable confidence in the results. The first method adopted consisted essentially in a comparison of the extrapolated scales given in terms of the effect of resistance on the resistance of several different metals. The metals chosen were iron, silver, and gold. Extrapolation of the results is complicated by the fact that the resistance changes of these metals are distinctly not of the first degree, nor even of the second degree within the errors of measurement. An ideal procedure would be to show that the same analytical expression represents the change of resistance as a function of pressure over the range up to 20000 that had formerly served to represent it up to 12000, assuming the linearity of the manganin over the entire range. One might feel considerable confidence if such an extrapolation were possible, because it would be highly improbable that deviations of all four metals would exactly conspire. As a matter of fact the situation could not be handled in quite this simple way, but this suggests the general idea of the method of approach. The details of the comparison will be found in the detailed presentation of data, and an estimate of the possible error of the linear extrapolation.

The second presumptive evidence as to the legitimacy of the extrapolation was obtained from the blank runs with pure iron. The results obtained from these runs were linear to a high degree of approximation at each of the five temperatures over the entire pressure range, with no hint of a change of trend between 12000 and 20000, so that for this additional reason considerable confidence may be felt in the extrapolation.

DETAILED DATA.

Resistance of Gold, Silver and Iron. As already stated, the primary purpose of these measurements was not to find how the resistance of these metals varies with pressure over the new pressure range, but rather to obtain some suggestion as to the legitimacy of measuring pressures above 12000 by assuming that the relation between pressure and the resistance of manganin, which had been shown by reference to a primary pressure gauge to be linear below 12000, continues to be linear between 12000 and 20000. For this purpose it was sufficient to make the measurements at a single temperature, 30° . The specimens measured were the identical samples which had been measured in 1917;⁴ they had been kept since that time in cork stoppered test tubes, and showed no perceptible change. The wires were double silk covered,

wound non-inductively into open coreless toroids; the resistance of gold, silver, and iron were respectively 18, 21, and 75 ohms. The three toroids, together with the manganin gauge, were attached one each to the four terminals of the four terminal plug, all coils being grounded in common to the cylinder. Measurements of resistance were made on the same Carey Foster bridge with which the pressure is regularly determined in terms of the change of resistance of the manganin.

It was not possible to get as clean cut results as had been hoped because of very perceptible hysteresis in the resistance of all three metals against manganin. Readings with increasing and decreasing pressure in all cases differed consistently by much more than the irregularity in the individual readings; the maximum differences between increasing and decreasing readings, in terms of the maximum change produced by pressure, were 0.74 per cent, 0.72 per cent, and 0.55 per cent, respectively, for gold, silver, and iron. Associated with the hysteresis were permanent changes of zero of the same order of magnitude. In view of the long period of rest since previous exposure to pressure, and the very elaborate seasoning of the manganin, and the further fact that the manganin did not show changes of zero, it is plausible to suppose that the hysteresis was not connected with the manganin, but with the other metals.

The mean resistance, that is the average with increasing and decreasing pressure, definitely could not be represented within the error of the readings by second degree relations in the pressure; but there were consistent departures always in the same direction, namely the maximum departure from linearity occurs at a pressure less than half the maximum pressure, and the curvature is greater at the low pressures than at the high pressures. The departures from a second degree relation were, however, in all cases slight, being greatest for iron, where the maximum departure of any observed point from that given by the second degree relation was 0.14 per cent of the maximum pressure effect. In view of the hysteresis, it did not seem worth while to attempt to reproduce the divergences by an analytical formula. The following are the second degree relations which best reproduce the actual results over the entire pressure range. The constants in these formulas are so chosen that the observed changes of resistance at 10000 and 20000 are exactly reproduced.

$$\text{Gold} \quad \frac{\Delta R}{R_0} = -3.017 \times 10^{-3} p + 1.05 \times 10^{-11} p^2$$

$$\text{Silver} \quad \frac{\Delta R}{R_0} = -3.575 \times 10^{-6}p + 1.90 \times 10^{-11}p^2$$

$$\text{Iron} \quad \frac{\Delta R}{R_0} = -2.377 \times 10^{-6}p + 0.71 \times 10^{-11}p^2$$

These results are all at 30° C, and pressure is in kg/cm².

The best comparison with previous results is afforded by comparing the fractional changes of resistance at 12000 obtained now with those obtained formerly. The present fractional changes at 12000 for gold, silver, and iron, respectively, are -0.0351, -0.0402, and -0.0275 against the previous values -0.0346, -0.0412, and -0.0275.

Finally the question of the possible error in the extrapolation was crudely answered in the following way. The best second degree curve was passed through the experimental points up to 12000, that is, the constants in a second degree relation were so determined as to give the observed changes of resistance at 6000 and 12000. With the constants so determined the change of resistance at 20000 was calculated and compared with the measured value, which of course involved the linear extrapolation of the manganin. The changes of resistance calculated in this way were too small by 1.58 per cent, 0.95 per cent, and 1.24 per cent for gold, silver, and iron respectively, which means that the pressure calculated from a second degree formula made to fit approximately the observed changes of resistance of gold, silver, and iron in the range of direct pressure measurement up to 12000 would give pressures too large at 20000 by the amounts mentioned. In view of the known failure of the second degree relation to exactly reproduce the results in the range up to 12000, the discrepancies just found must be very generous upper limits to the true error; and I believe that we may finally conclude that the pressure obtained by a linear extrapolation of the manganin resistance is probably in error at 20000 by not more than a small fraction of one per cent.

Resistance of Black Phosphorus. This material was from a batch freshly prepared in the conventional way from white phosphorus at 200° C and 12000 kg/cm², the pressure transmitting medium being water. The original dimensions of the white phosphorus were 1.4 cm diameter and 10 cm long. The transition is accompanied by a 33 per cent decrease of volume. The structure of the resulting black phosphorus is coarsely granular at the upper end and at the lower end very fine grained and distinctly filamentary in character, the direction of the filaments presumably being the direction of relative motion

during the transition. The fracture at the lower end is very similar to that of hematite in the form of the so-called "pencil ore." The specimen was cut from the lower end; some selection was necessary in order to obtain a piece free from cracks. The specimen was in the form of a rod of rectangular section, 2.1×1.7 mm, and about 2.5 cm total length. Measurements were made by the potentiometer method, using four terminals. The distance between potential terminals was 1.36 cm. The current terminals were bands completely girdling the specimen and making approximately uniform contact all around, so as to minimize end effects.

The specific resistance at 30° C at atmospheric pressure was 0.484 ohm cm; this is somewhat smaller than two values previously found which were 0.588 and 0.773.⁵ The difference is perhaps not more than might be expected in view of the pronounced structural differences of different specimens. The temperature coefficient at atmospheric pressure is negative, the resistance at 75° being 35 per cent less than at 30° . This is not very different from the temperature coefficient shown by the two previous samples; the temperature coefficient varies less from sample to sample than does the specific resistance itself.

Two unsuccessful attempts to determine the pressure effect were made before the final successful attempt; one of these was terminated by rupture of the cylinder and the other by rupture of the insulating plug. The partial results obtained during the unsuccessful attempts were not inconsistent with those finally obtained. Successful runs were made at 30° and 75° . The initial application of pressure at 30° was accompanied by seasoning effects, the readings with decreasing pressure falling below those with increasing pressure and the zero resistance being permanently depressed by 16 per cent. The seasoning was practically complete with the first application of pressure; on the second application points agreed with increasing and decreasing pressure, the zero shift was only 0.5 per cent, and no point lay off a smooth curve by more than 2.3 per cent of the resistance at that point, the average deviation being much less. The basis of estimation of the smoothness of the results is necessarily different here from that usually employed because of the very large changes of resistance; the meaning of the statement just made is that when $\log_{10} R/R_0$ is plotted against pressure the maximum deviation from a smooth curve of any single point was 0.01, the total variation in the logarithm being more than 2.00. $\log R/R_0$ is given as a function of pressure at 30° and 75° in Table I.

TABLE I.
RESISTANCE OF BLACK PHOSPHORUS.

Pressure kg/cm ²	Log ₁₀ R/R ₀		Pressure kg/cm ²	Log ₁₀ R/R ₀	
	30°	75°		30°	75°
0	0.000	9.871	11000	8.687	8.677
1000	9.894	9.762	12000	8.554	8.554
2000	9.787	9.655	13000	8.424	8.439
3000	9.678	9.548	14000	8.298	8.325
4000	9.566	9.441	15000	8.182	8.217
5000	9.451	9.333	16000	8.078	8.118
6000	9.332	9.223	17000	7.994	8.037
7000	9.209	9.112	18000	7.920	7.971
8000	9.083	9.001	19000	7.875	7.920
9000	8.953	8.890	20000	7.838	7.883
10000	8.820	8.779			

Previously measurements have been made of the resistance of black phosphorus up to 12000 at 0°, 50°, and 100°. In the range common to the two sets of measurements the results are not dissimilar. Thus at 30° and 12000 kg/cm² the previous sample showed a decrease of resistance to 0.0333 of its initial value, whereas the resistance of the present sample under the same conditions decreases to 0.0358. The pressure coefficients and the temperature coefficients thus both agree much more closely than the specific resistances.

Three special features of the resistance require comment. In the first place there is the very large decrease of resistance, at 0° and 20000 kg/cm² the resistance being only 0.0069 of its initial value. In the second place there is the fact that the relative decrease is less at higher temperatures, and by so large an amount that the curves of actual resistance cross at about 12000. Above 12000 the temperature coefficient reverses sign and becomes positive. This decrease of temperature coefficient with rising pressure was also found formerly, but the effect was not so large, and the coefficient had not yet reversed sign up to the previous maximum of 12000. In the third place there is the complicated variation of pressure coefficient with pressure at constant temperature, and particularly the very rapid change of slope at high pressures. This is shown in Figure 2, in which is plotted the differences of log R/R₀ for pressure differences of 1000 kg/cm². Unless there is some very abrupt reversal of trend at pressures only a

little above 20000, a smooth and relatively short extrapolation demands that the pressure coefficient reverse sign at about 23000, so that above 23000 the resistance may be expected to increase with rising pressure at constant temperature. Such a minimum of resist-

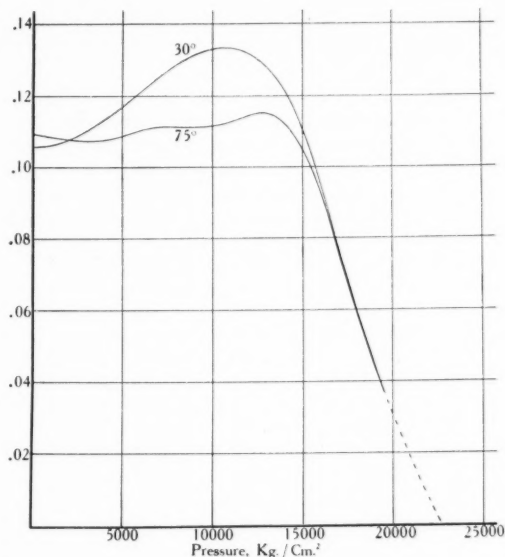


FIGURE 2. The first differences for pressure intervals of 1000 kg/cm² of $\log_{10} R/R_0$ of black phosphorus as a function of pressure at 30° and 75° C. The dotted part of the curve is extrapolated.

ance has been established up till now only for some of the alkali metals and for barium.⁶

Resistance of Tellurium. This material is of interest because of the very large effect of pressure on resistance. It had previously been measured at -183° and -78° up to 7000 kg/cm², and at 0° and 95° up to 12000.⁷ Measurements were now made at 30° and 75° up to 20000 on the identical specimens formerly used. There was no hysteresis in the readings nor permanent changes of zero after exposure to pressure. The readings at 30° C on the specimen with length

inclined at 23.5° to the trigonal axis were the most irregular, the greatest departure of any single point being 0.02 on a logarithmic scale. The maximum departure of any point on the three other isotherms was less than 0.01, and the average deviation from smoothness perhaps 0.002.

Smoothed results for $\log_{10} R/R_0$ as a function of pressure and temperature for the two orientations are given in Table II. The first

TABLE II.
RESISTANCE OF SINGLE CRYSTAL TELLURIUM.

Pressure kg/cm ²	Log R/R_0			
	23.5° orientation		86° orientation	
	30°	75°	30°	75°
0	0.000	9.704	0.000	9.697
1000	9.853	9.548	9.844	9.532
2000	9.709	9.405	9.691	9.377
3000	9.568	9.271	9.541	9.231
4000	9.430	9.145	9.395	9.094
5000	9.295	9.025	9.254	8.964
6000	9.165	8.910	9.119	8.841
7000	9.040	8.800	8.989	8.725
8000	8.921	8.693	8.865	8.615
9000	8.809	8.591	8.747	8.510
10000	8.705	8.496	8.634	8.410
11000	8.605	8.405	8.526	8.316
12000	8.510	8.318	8.423	8.227
13000	8.419	8.237	8.324	8.142
14000	8.332	8.161	8.230	8.061
15000	8.249	8.089	8.140	7.983
16000	8.170	8.022	8.053	7.908
17000	8.095	7.958	7.969	7.836
18000	8.025	7.898	7.891	7.768
19000	7.959	7.841	7.818	7.704
20000	7.897	7.789	7.752	7.644

differences for thousand kilogram intervals are shown in Figures 3 and 4. An exact comparison with previous results is not possible because the temperatures of the two sets of readings were not the same, and resistance is far from a simple function of temperature, as

Figures 2 and 3 of the former paper show. The best that can be done is to make comparison at the two temperatures most nearly equal, namely 75° and 95° . The former results may be reduced to 75° by linear interpolation between 0° and 95° , and the present results reduced to 95° by linear extrapolation from 30° and 75° , and the average taken of the two discrepancies thus obtained. In this way it may be found that the logarithm of relative resistance at 12000 given by the present

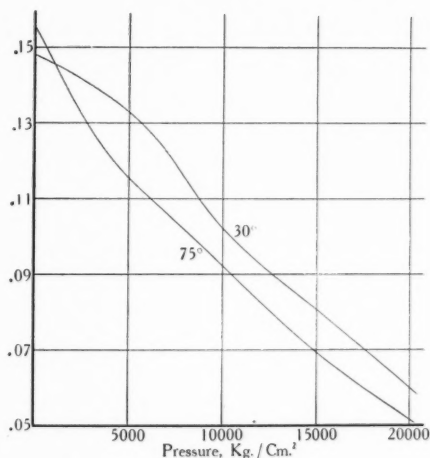


FIGURE 3. The first differences for pressure intervals of 1000 kg/cm² of $\log_{10} R/R_0$ of single crystal tellurium, the length of the rod inclined at 23.5° to the trigonal axis, as a function of pressure at 30° and 75° C.

set of measurements differs for both orientations by about 0.03 from that previously found, the direction of the difference being such that the changes of resistance with pressure are now greater than formerly. Such a discrepancy is beyond experimental error, and indicates that some permanent change has taken place in the specimen during the 17 months since the former measurements. This change is not important, however, in view of the very large change in resistance produced by pressure, the total change in $\log R/R_0$ at 20000 being about 2.2.

The Table and the Figures show that the pressure effect is not

greatly dependent on the orientation, the variation being much less than for some more highly metallic materials. One might perhaps be prepared to find a large dependence on orientation in view of the pronouncedly crystalline character of tellurium with its very marked cleavage. The results suggest that the electrical properties are not

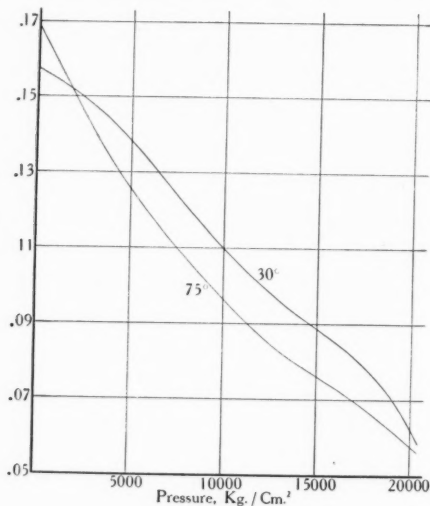


FIGURE 4. The first differences for pressure intervals of 1000 kg/cm² of $\log_{10} R/R_0$ of single crystal tellurium, the length of the rod inclined at 86° to the trigonal axis, as a function of pressure at 30° and 75° C.

greatly affected by the crystal structure, a result which is perhaps to be correlated with the non-metallic character of tellurium.

Apart from the orientation effects, tellurium shows two of the striking effects of black phosphorus, although in less marked degree. There is in the first place a drawing together of the curves for different temperatures as pressure increases, the temperature coefficient at 20000 being only about one third as great as at atmospheric pressure. The temperature coefficient beyond 3000 drops nearly linearly with pressure; linear extrapolation indicates a reversal of sign of temperature coefficient at somewhat less than 30000. In the second place

there is also a large decrease of pressure coefficient with increasing pressure, as shown in Figures 3 and 4. Because of the irregularity of these curves, extrapolation is more hazardous than extrapolation of the temperature coefficient, but a rough linear extrapolation indicates also a reversal of sign of pressure coefficient probably not far from 30000 and somewhat above it. That is, at pressures somewhat above 30000 resistance may be expected to increase with increasing pressure.

The total drop of relative resistance is about the same at 20000 for tellurium and black phosphorus; the relative resistance of tellurium at the points where temperature and pressure coefficients reverse sign will, therefore, be markedly less for tellurium than for black phosphorus.

Resistance of Copper Sulphide. This substance belongs to the class of semi-conductors, about which we have very little information with regard to behavior under pressure. The source of the material was Kahlbaum, "crystallized" fused lumps. A rod 0.35 cm in diameter and 1.21 cm long between potential terminals was formed by grinding and turning from one of the homogeneous lumps. Connections were spring clips of 0.008 inch steel wire, embracing the rod and pressing against opposite ends of a diameter in a small groove of V section cut around the rod. Measurements were made by the regular potentiometer method; the measuring current was about 0.1 amp. The measurements were never as definite with this material as with the metals; readings were not always perfectly steady, and on reversing current there were transient effects which took an unusually long time to disappear, although the final resistance for the two directions of current flow were usually close together. The irregular effects were much more prominent at 75° than at 30°.

The specific resistance at atmospheric pressure at 30° was 0.000818 ohm cm, and the average temperature coefficient of resistance between 0° and 100°, calculated by linear extrapolation of readings at 30° and 75° was -0.00686 .

The relative resistances as a function of pressure at 30° and 75° are plotted in Figure 5. At 30° the resistance is roughly a single valued function of pressure, without hysteresis between increasing and decreasing pressure. There is a sharp change in direction at 3000 kg/cm², where the resistance is about 0.95 its initial value. Above 3000 the rate of decrease of resistance with pressure suddenly becomes about ten times less; as pressure increases beyond 3000, however, this diminished rate becomes larger again, giving a curve for resistance

against pressure concave toward the pressure axis, an abnormal effect shown by very few substances. At 75° on the first application of pressure, the same qualitative situation was again found, the discontinuity in slope now being displaced to about 2000, and at pressures above this the curve again being concave toward the pressure axis. At 75° it is evident however that there is an additional irreversible phenomenon; this seems to have been initiated between 10000 and 12000 with increasing pressure and to have progressed so

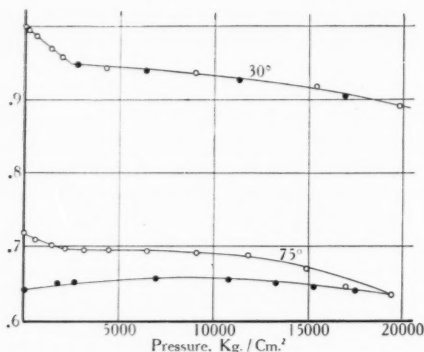


FIGURE 5. The relative resistance of Cu_2S as a function of pressure at 30° and 75° C. The open circles represent readings made with increasing pressure and the solid circles with decreasing pressure.

far by the time that 2000 was again reached with decreasing pressure that the expected discontinuity at this point was suppressed. The points shown in the figure for decreasing pressure do not represent complete equilibrium, but at each point there was a slow creep of resistance downwards which had not entirely ceased when the reading was recorded. After the final reading at 75° the resistance at atmospheric pressure at 30° was redetermined, and was found to be displaced downward by almost exactly the amount of the total zero displacement at 75° . The internal change is, therefore, very much retarded if indeed not entirely inhibited at atmospheric pressure.

This substance should evidently be studied further; in particular the compressibility should be measured and also measurements made on material from other sources.

Compression and Thermal Expansion of Lithium. Many of the details of the measurements have already been described in the section on Apparatus and Technique. The source of the material was Kahlbaum. It was melted under Nujol in pyrex, taking great pains to keep the temperature as near the melting point as possible in order to avoid chemical attack on the glass. It was then filtered in the liquid state by forcing through a small aperture, cast into a rod of somewhat greater than the final diameter, and then extruded to the final diameter of 6 mm. The length of the sample as mounted in the piezometer was 5.9 cm. Two different sorts of measurements were made. The first was of the isotherms at 0°, 30°, and 75°. From these measurements good values of the compression at 0° were obtained, but the difference between isotherms was not accurate enough to yield good values for the thermal expansion. The second set-up yielded thermal expansion at approximately 5000, 10000, 15000, and 20000; it also yielded rough values for the isothermal compression at 0° which checked with the better values yielded by the other method with a maximum discrepancy of 4 per cent at the maximum pressure. The maximum departure of any point of the isotherm at 0° from a smooth curve corresponded to 0.4 per cent of the maximum change of volume at 20000. The irregularity in the individual determinations of thermal expansion corresponded to a probable error in the final results of the order of 1 per cent on the thermal expansion itself. Since the measurements were made at five temperatures, the thermal expansions as directly calculated give the thermal expansion as a function of the temperature range. The measurements were not accurate enough, however, to justify the attempt to specify the thermal expansion at any fixed pressure as a function of temperature range. It is true that the thermal expansion in the lower range, 0° to 30°, was consistently lower than that for any of the higher ranges, and this, taken at its face value, is evidence of an increase of thermal expansion with increasing temperature. However, the accuracy over the shorter ranges is less than that over the wider ranges, and since the expansion over the wider ranges did not vary consistently with temperature, too great significance should not be attached to the consistent behavior of the lower range. I believe it probable, however, that there is a slight increase of thermal expansion with temperature in the range of the measurements, and that the reversal of sign of $\left(\frac{\partial^2 v}{\partial \tau^2}\right)_p$ exhibited by all liquids hitherto measured does not occur in lithium in the present

range. The thermal expansion tabulated in the following is the mean expansion obtained by taking a weighted average of the individual results for the ranges $0-30^\circ$, $0-52.5^\circ$, $0-75^\circ$, and $0-95^\circ$, weighting these roughly 1, 2, 3, 4. The experimental values of the weighted mean expansions are shown in Figure 6; the value at atmospheric

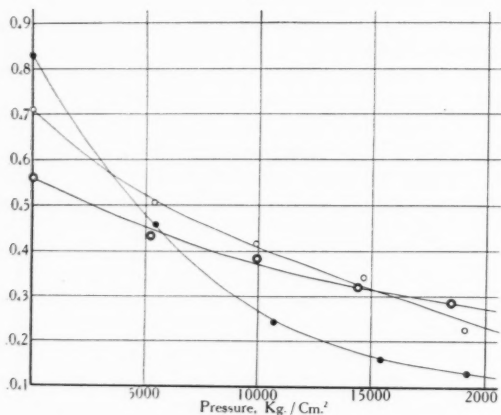


FIGURE 6. The mean linear thermal expansion between 0° and 95° C of lithium, sodium, and potassium as a function of pressure. The double open circles are the observed values for lithium, the single open circles for sodium, and the solid circles for potassium.

pressure was taken from I. C. T. The values listed in Table III were read from the smooth curve of Figure 6. These thermal expansions are calculated on the original length at 0° C and atmospheric pressure.

The volume compression at 0° listed in Table III may be compared with that formerly obtained.⁸ Comparison at 10000 will sufficiently indicate the order of the agreement; the present value for $\Delta V/V_0$ is 0.0739; the former value, obtained by linear extrapolation of the determinations at 30° and 75° , and correcting the reduction from $\Delta l/l_0$ to $\Delta V/V_0$, was 0.0725. The former published value, with the incorrect reduction from Δl to ΔV was 0.0759. The mean linear thermal expansion at 10000, deduced from the former measurements after correcting the reduction from Δl to ΔV was 0.000044, against 0.000037 found now.

The former results can be represented over the pressure range up to 12000 by a formula of the second degree. Over the extended range up to 20000 a second degree expression is not quite adequate within experimental error, although it is adequate within two or three units in the last place. A second degree expression giving the correct

TABLE III.
VOLUME COMPRESSION AND THERMAL EXPANSION OF LITHIUM.

Pressure kg/cm ²	Volume Compression - $\Delta V/V_0$ at 0° C	Mean Linear Thermal Expansion 0°-95° C
0		(000056)
2000	.0164	51 _s
4000	.0320	47 _s
6000	.0466	43 _t
8000	.0606	40 _o
10000	.0739	37 _o
12000	.0866	34 _s
14000	.0984	32 _s
16000	.1094	30 _o
18000	.1198	28 _s
20000	.1296	27 _s

$\Delta V/V_0$ at 10000 and 20000 gives too small Δv 's below 10000 and too large Δv 's between 10000 and 20000.

Compression and Thermal Expansion of Sodium. The source of the material was Kahlbaum; it was filtered, cast, and extruded to the final dimensions. The length was 2.5 cm; two different diameters were used; 6 mm for the first runs giving isothermal compression, but for the thermal expansion measurements, where it was essential to secure the greatest possible freedom from distortion, the diameter was increased to 8.7 mm.

Most of the preliminary work in perfecting the final details was done with sodium; in all, the apparatus was set up with fifteen different fillings of sodium, and fifteen complete or partial runs were made. A number of different measurements of isotherms at different temperatures were made in the endeavor to determine the thermal expansion by taking the difference of complete isotherms, and at least four of these runs were good enough to yield values for the isothermal compression at 0°. The values given in the following were the mean of

these four determinations; at both 10000 and 20000 the extreme departure from the mean of the four individual determinations was 0.22 per cent of the maximum effect. The thermal expansions tabulated in the following were obtained from a single set-up after the final method had been worked out; the self consistency of the thermal expansion over the different ranges of temperature was about the same as for lithium, although the irregularity was somewhat greater. No consistent variation of thermal expansion with temperature was found, and in the following only the mean values are given, weighted for range, as already explained.

In Table IV are shown the volume compression at 0° and the mean

TABLE IV.
VOLUME COMPRESSION AND THERMAL EXPANSION OF SODIUM.

Pressure kg/cm ²	Volume Compression - $\Delta V/V_0$ at 0° C	Mean Linear Thermal Expansion 0°-95° C
0		(.000071)
2000	.0295	62 ₂
4000	.0552	55 ₃
6000	.0779	49 ₈
8000	.0981	45 ₀
10000	.1165	40 ₈
12000	.1332	37 ₀
14000	.1488	33 ₇
16000	.1632	30 ₀
18000	.1767	26 ₆
20000	.1894	23 ₃

linear thermal expansion obtained from the smooth curve of Figure 6 drawn through the experimental points.

The general character of the agreement with the results previously obtained⁹ is sufficiently indicated by a comparison of the results at 10000. Linear extrapolation to 0° of the results previously obtained at 30° and 75°, making the correct reduction from $\Delta l/l_0$ to $\Delta V/V_0$ gives $\Delta V/V_0$ at 0° and 10000 kg/cm² equal to 0.1134, against 0.1165 found now. The previous published value, in which the reduction was incorrectly made, was 0.1228. The mean thermal expansion at 10000, to be deduced from the former results, correctly reduced, was

0.000034 against 0.000041 found now. There is no question but that the present value is to be preferred.

Compression and Thermal Expansion of Potassium. The material was obtained from Kahlbaum. It was melted under Nujol, filtered through a fine hole, cast into a coherent perfectly clean rod of diameter somewhat greater than the final diameter, and reduced to the diameter of the finished specimen by extrusion. The final diameter was 0.87 cm and the length 1.77 cm. More or less complete runs were made with six different set-ups of the apparatus. The first of these was

TABLE V.
VOLUME COMPRESSION AND THERMAL EXPANSION OF POTASSIUM.

Pressure kg/cm ²	Volume Compression $-\Delta V/V_0$ at 0° C	Mean Linear Thermal Expansion 0°-95° C
0		(.000083)
2000	.0571	67 ₀
4000	.1002	53 _s
6000	.1347	42 ₇
8000	.1640	33 _s
10000	.1890	26 ₀
12000	.2108	22 ₀
14000	.2300	18 _s
16000	.2472	15 _s
18000	.2626	13 _s
20000	.2767	12 _s

terminated by an explosion after a fairly complete determination of three isotherms; the results of four others were not sufficiently good to calculate, irregularities being due both to fluctuations in the gauge and to mechanical distortion of the specimen, which is particularly hard to avoid with potassium because of its great softness. The final run gave satisfactory results both for the isotherm at 0° and for the thermal expansion at four approximately constant pressures.

The volume compression at 0° and the linear thermal expansion are given in Table V. The volume compressions so tabulated are the weighted means of the two successful isotherms at 0°, giving the results with the two runs a weight inversely as the average departure of the readings from a smooth curve. These departures were 0.0034 and 0.0015, expressed as fractional parts of the total effect, the

second run giving the best results. The difference between the results of the two runs, expressed as a fraction of the maximum effect, was 2 per cent at 10000 and 1.8 per cent at 20000, the better run giving the lower values for decrease of volume.

The thermal expansions given in Table V were obtained from the smooth curve of Figure 6, drawn through points representing the mean of the results for the four temperature ranges, weighted as already described. There was no consistent variation of thermal expansion with temperature at constant pressure, and it appears to be justified to retain only the weighted mean in the final results. The measured displacements at the high pressure end of the range, from which the thermal expansions were calculated, were smaller than for the two other alkalis, both because of the shorter length of the specimen and because of the absolutely smaller value of the thermal expansion. This was reflected in a greater irregularity of the results for the four temperature ranges; the apparently greater regularity of the experimental points for potassium as compared with sodium shown in Figure 6 is probably to a certain extent fortuitous.

The volume compression was previously determined only at 45° and up to 12000.¹⁰ Using the value for the thermal expansion found now in order to extrapolate from 45° to 0°, and correcting the reduction from Δl to ΔV , the volume compression at 10000 formerly found was 0.1877, against 0.1892 found now. The published value, in which Δl was incorrectly reduced to ΔV , was 0.2150. The discrepancy due to the incorrect reduction is at its maximum for potassium, since it increases at an accelerated rate with increase of $\Delta V/V_0$.

The mean thermal expansion formerly found at 10000 was 0.000020, against 0.000027 found now. In general, the new values are better than the former values.

DISCUSSION.

The principal points with regard to electrical resistance have already been discussed in the detailed presentation of data. In general comment, the resistance of black phosphorus and tellurium approaches that of the metals in so far as the reversal of sign of the temperature coefficient is concerned. If the reversal of sign of the pressure coefficient is considered to be a characteristic of all metals, as it is known to be for the alkali metals, then it is highly probable that black phosphorus and tellurium are metallic in this respect also at pressures not far beyond those actually reached. But the absolute value of the specific resistance, even at the highest pressures, still remains in the

non-metallic range, being, for example, 20 times greater for tellurium at 20000 kg/cm² than for bismuth under normal conditions.

With regard to the alkali metals, it is to be remarked in the first place that there are none of the abnormalities in compressibility at high pressures, particularly for potassium, which were previously found and which were entirely due to the erroneous reduction from $\Delta l/l_0$ to $\Delta V/V_0$. The two compressibilities $\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_\tau$ and $\frac{1}{v_0} \left(\frac{\partial v}{\partial p} \right)_\tau$ both decrease smoothly with pressure, even for potassium, up to the highest pressure. For potassium the "instantaneous" compressibility, $\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_\tau$, has dropped at 20000 to about one third its value at atmospheric pressure, and the "actual" compressibility, $\frac{1}{v_0} \left(\frac{\partial v}{\partial p} \right)_\tau$, to about one quarter its initial value. Furthermore, there is now no crossing of the compressibility curves, but both "instantaneous" and "actual" compressibility increase from lithium to sodium to potassium over the entire range of pressure.

The thermal expansions, however, do show reversals of order. The thermal expansion drops with increasing pressure by a factor which increases from lithium to sodium to potassium, and the increase is more than sufficient to wipe out the initial superiority of potassium. The result is that above 3500 kg/cm² the expansion of sodium is greater than that of potassium, and above 15000 it is less than that of lithium, and above 5700 the expansion of potassium is less than that of lithium. This means that above 15000 the order of the alkali metals, arranged according to decreasing thermal expansion is: lithium, sodium, potassium; exactly the reverse of the order at atmospheric pressure. One is strongly reminded of the reversal of the order of the melting points of the alkali metals at high pressures already found; the two phenomena are doubtless intimately related.

Another feature is that the thermal expansion at 20000 of all three metals has dropped by a materially larger factor than has the compressibility. This is the exact reverse of the behavior usually found with organic liquids, the compressibility of which in the range up to 12000 decreases by a factor two or three times greater than the factor of decrease of thermal expansion.

A knowledge of thermal expansion is involved in an interesting speculation of G. N. Lewis as to limiting behavior at infinitely high pressure. Lewis has suggested¹¹ that it may be that the entropy of a

crystalline phase tends toward zero at infinite pressure at all temperatures. In virtue of the thermodynamic relation $\left(\frac{\partial s}{\partial p}\right)_\tau = -\left(\frac{\partial v}{\partial \tau}\right)_p$

we have:
$$S(0, \tau) - S(p, \tau) = \int_0^p \left(\frac{\partial v}{\partial \tau}\right)_p dp.$$

$S(0, \tau)$ may be determined by measurements at atmospheric pressure of specific heat as a function of temperature, assuming in accordance with the third law that entropy at 0° Abs vanishes. $S(0, \tau)$ has been so determined for a large number of substances and may be found in

I. C. T. Lewis's hypothesis then demands that $\int_0^p \left(\frac{\partial v}{\partial \tau}\right)_p dp$ cannot

be larger than $S(0, \tau)$, so that $\left(\frac{\partial v}{\partial \tau}\right)_p$ must decrease with increasing pressure fast enough to fulfill this condition. The integral may be approximately evaluated graphically. The result for potassium is that

$$S(0, 0^\circ \text{C}) - S(20000, 0^\circ \text{C}) = 2.03 \text{ kg cm}^\circ\text{C gm}.$$

The value given in I. C. T. for $S(0, 0^\circ \text{C})$ is 17.3 in the same units. Similarly for sodium $S(0, 0^\circ \text{C}) - S(20000, 0^\circ \text{C}) = 2.56 \text{ kg cm}^\circ\text{C gm}$, and $S(0, 0^\circ \text{C}) = 22.1$. The value for $S(0, 0^\circ \text{C})$ is not tabulated for lithium, so that there was no particular point in calculating the change of entropy out to 20000; it is evident from the graph that it will be between that of sodium and potassium. The conclusion for sodium and potassium is that the change of entropy with pressure at 20000 at 0°C falls by a factor of about 8.5 to reach the theoretical limiting value. The state of zero entropy at 0°C must then occur at excessively high pressures. Even if $\left(\frac{\partial v}{\partial \tau}\right)_p$ for potassium should remain constant beyond 20000, zero entropy would not be reached below a pressure of 450,000 kg/cm². The general conclusion is that the zero state of entropy at ordinary temperatures is so very remote as probably not to impose any useful restriction on speculations as to behavior in the experimental range.

With the more accurate values of thermal expansion now available, it is possible to calculate more accurately than before the pressure at which the internal energy passes through its minimum with increasing pressure at constant temperature. Since $\left(\frac{\partial E}{\partial p}\right)_\tau = -\tau \left(\frac{\partial v}{\partial \tau}\right)_p -$

$p \left(\frac{\partial v}{\partial p} \right)_\tau$, this pressure is given by $p = -\tau \frac{\partial v}{\partial \tau} / \frac{\partial v}{\partial p}$. Probably the easiest way to find this pressure is to plot $\tau \frac{\partial v}{\partial \tau}$ and $-p \frac{\partial \tau}{\partial p}$ against pres-

sure and determine the point of intersection of the curves. It was found in this way that at 0° C the minimum energy of lithium occurs at about 5000 kg/cm², that of sodium at 4000, and that of potassium at 2300. These pressures are much lower than the corresponding pressures for harder metals such as iron, and furthermore are somewhat lower than obtained previously on the basis of earlier values of thermal expansion. The volume at which internal energy passes through a minimum is roughly the volume at which mean attractive and repulsive forces are in equilibrium, and this again should be roughly the same as the volume at 0° K at atmospheric pressure. This latter volume has not been determined with much accuracy, but there seems to be no question but that it is significantly larger than the volume at 0° C at the pressure of the minimum of internal energy. This seems to be the universal rule, and is doubtless connected with the compression of the force fields of the atom by external pressure.

At pressures beyond the minimum of internal energy the term $-p \frac{\partial v}{\partial p}$ becomes increasingly dominant over $\tau \frac{\partial v}{\partial \tau}$, so that at the highest pressures nearly all the mechanical work of compression is permanently retained as increase of internal energy, the energy flowing out as heat to compensate for the temperature rise produced by the compression becoming unimportant. This phenomenon is most marked, of course, with potassium; at 20000 kg/cm² all except 8 per cent of the mechanical work of compression is permanently retained. I have calculated approximately the total increase of internal energy of potassium at 0° C up to 20000 kg/cm² by a simple graphical integration, and it proves to be about 14.5 kg m for that amount of potassium which occupies 1 cm³ at 0° C at atmospheric pressure. The total mechanical work of compression of the average organic liquid is not far from this.

SUMMARY.

The modifications in technique necessary in extending the pressure range from 12000 to 20000 kg/cm² are described.

The electrical resistance of silver, gold, and iron is found to extrapolate smoothly from 12000 to 20000, in such a way as to make it very

probable that the manganin resistance gauge may be safely used up to 20000 kg/cm², assuming a linear relation between pressure and change of resistance, and obtaining the pressure coefficient from a single calibration at 7640 kg/cm², with a maximum error of a few tenths of one per cent.

The electrical resistance of black phosphorus and of single crystal tellurium in the 23.5° and 86° orientations is measured to 20000 at 30° and 75° C. Both of these substances show very large decreases of resistance, the resistance at 20000 being less than 0.01 of its value at atmospheric pressure. The temperature coefficient of black phosphorus reverses sign near 12000 kg/cm², and above 12000 is positive, like that of the metals. The temperature coefficient of tellurium (both orientations) also decreases markedly with pressure, but does not reverse sign, having a value at 20000 kg/cm² about one third of its value at atmospheric pressure. The rate of decrease of resistance with pressure drops very markedly with increasing pressure. With black phosphorus the drop is so rapid that a short extrapolation indicates that the resistance will probably pass through a minimum between 23000 and 24000 kg/cm². The extrapolation for tellurium is not so certain, but it is probable that at a pressure not much above 30000 its resistance will also pass through a minimum.

The resistance of Cu₂S at 30° decreases with pressure, with a discontinuity in the direction of change near 2500 kg/cm², above 2500 the rate of decrease being only about one tenth as large as immediately below 2500. Above 2500 the curve of resistance against pressure is concave toward the pressure axis, a very unusual phenomenon. The phenomena at 30° are approximately reversible. At 75° the same qualitative features as at 30° are shown on the first application of pressure, but above 10000 irreversible changes begin to take place, and the resistance with decreasing pressure does not retrace its former path, but lies below it, and the low pressure discontinuity is suppressed.

The change of volume of lithium, sodium, and potassium is measured at 0° C. The compressibility of these three metals drops smoothly, both with respect to pressure and with respect to each other, over the entire range. The relative drop of the compressibility of potassium is the greatest and that of lithium the least; at atmospheric pressure the compressibility of potassium is three times that of lithium and at 20000 kg/cm² 1.65 times.

The mean linear expansion between 0° and 95° C of the three alkali metals has been determined up to 20000 kg/cm². The expansion

drops with increasing pressure by a factor considerably larger than does the compressibility. The drop for potassium is so much greater than that for sodium and lithium that there is a crossing of the curves, with the result that at 20000 kg/cm² the order of the expansions of lithium, sodium, and potassium is exactly the reverse of what it is at atmospheric pressure, potassium at 20000 appearing as the "hardest" and lithium as the "softest" metal. The same phenomenon is shown by the melting points.

The decrease of entropy of these three metals with pressure at constant temperature may be evaluated in terms of the thermal expansions. It appears that any vanishing of the entropy must occur at pressures excessively beyond the present experimental range.

I am indebted to my assistant Mr. L. H. Abbot for making the readings, which have often demanded a high degree of skill, to the Rumford Fund of the American Academy of Arts and Sciences for financial assistance in purchasing supplies, and to the Francis Barrett Daniels Fund of Harvard University for financial assistance with respect to the salary of Mr. Abbot.

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- ⁸ First reference under 2, page 202.
- ⁹ First reference under 2, page 203.
- ¹⁰ First reference under 2, page 206.
- ¹¹ G. N. Lewis, ZS. f. Phys. Chem. **130**, 532, 1927.

1. The first part of the paper is devoted to a discussion of the

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